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Signed Andrew Gray

Dated 15 November 1999

Patents Form 1/77

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Cardiff Road
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1. Your reference — SMC 60340/GB/P

2. Patent application number *(The Patent Office will fill in this part)* — 0 4 FEB 1999 — **9902386.3**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Zeneca Limited
15 Stanhope Gate
London
W1Y 6LN

Patents ADP number *(if you know it)* — 6254007002

If the applicant is a corporate body, give the country/state of its incorporation — United Kingdom

4. Title of the invention — Printing Inks

5. Name of your agent *(if you have one)*

FAWKES, David Melville

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Zeneca Specialties
Hexagon House
PO Box 42
Blackley
Manchester M9 8ZS

Patents ADP number *(if you know it)* — 2180511002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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Patents Form 1/77

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Description	9
Claim(s)	2
Abstract	
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Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature C Terry Date 3 February 1994

Zeneca Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

K.M.Pinder/G.Terry 0161 721 1361/2

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PRINTING INKS

The present invention relates to non-aqueous printing inks containing pigments and their use in "drop-on-demand" ink jet printers.

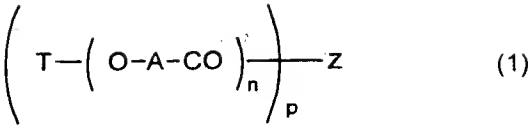
One of the most important class of ink jet printers is the so-called "drop-on-demand" (hereinafter DOD) printer, where droplets of ink are expelled from a print head to make a print mark only when desired to form an image during the printing process. DOD printers use either an electrostatically accelerated ink jet or sequence of droplets which are ejected by pressure impulse actuation. In the latter type of DOD printer, each ink droplet is individually ejected from a nozzle in the print head by means of pressure pulses which are induced, for example, by a piezo-electric actuator acting on the ink in a channel supplying the nozzle or by generation of a vapour bubble in response to a thermal pulse.

One particular problem encountered in continuous printing with ink jet printers is that a small amount of the tail of the droplet being ejected tends to separate from the droplet and collect on that part of the surface of the print head immediately surrounding the nozzle. With high speed printers, there is less opportunity for this tail of the droplet to recede back into the nozzle before the next pressure pulse which results in the build up of an ink residue on the surface of the print head giving a distorted printed mark. This is particularly marked in high dot density printers and especially colour printers. This has led to the introduction of coatings for the print head to reduce the accumulation of such residues but even so the print head still requires cleaning resulting in down-time of the printer.

Improved print performance in DOD printers has been sought by advances in printing ink formulations. Thus, WO 97/15633 discloses a printing ink containing a pigment which is dispersed in a non-aqueous medium using a polyester amine dispersant where some of the basic amine groups in the dispersant are neutralised with an acid or acidic phenolic compound. These printing inks are stated to exhibit a reduction in the amount of residual ink which forms on the print head at the end of each pulse by improving the rate at which the tail of the droplet retreats into the nozzle of the print head. One method of determining the propensity of an ink droplet to retreat back into the nozzle is to measure the Receding Meniscus Velocity (hereinafter RMV) of the printing ink on a surface, such as a fluorosilane coated metal surface. One such method of measuring RMV is described in WO 97/15633.

It has now been found that printing inks exhibiting a superior RMV can be made by dispersing a pigment in a non-aqueous medium by means of a dispersant containing a higher proportion of polyester to those described in WO 97/15633.

According to a first aspect of the present invention there is provided a drop on demand ink jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of Formula (1)



(1)

wherein

T is hydrogen or a polymerisation terminating group;

A is C_{8-20}-linear alkylene or alkenylene;

Z is the residue of a polyamine or polyimine;

n is from 2 to 10;

p is not less than 2; and

the weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is from 5:1 to 20:1; including salts thereof.

The dispersant of Formula 1 is hereinafter referred to as The Dispersant.

When T is a polymerisation terminating group, it is preferably the residue of a carboxylic acid of formula T-COOH wherein T is aliphatic which may be linear or branched, saturated or unsaturated but is preferably linear and preferably saturated. The number of carbon atoms in T can be as high as 50. It is preferred that T contains not less than 8, more preferably not less than 12 and especially not less than 14 carbon atoms. It is also preferred that T contains not greater than 30, preferably not greater than 25 and especially not greater than 20 carbon atoms.

Preferably, A contains not less than 10, more preferably not less than 12 and especially not less than 14 carbon atoms.

The integer n is preferably not less than 3 and especially not less than 4. It is also preferred that n is not greater than 8 and especially not greater than 6.

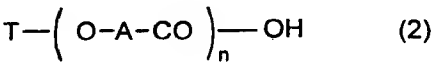
The integer p is preferably not greater than 2000 and especially not greater than 1000.

Z is preferably the residue of polyallylamine, polyvinylamine, more preferably poly(C_{2-4}-alkyleneimine) (hereinafter PAI) and particularly poly(ethyleneimine) (PEI).

The PAI may be linear or more preferably branched.

The polyamine or polyimine preferably has a number-average molecular weight from 500 to 600,000, more preferably from 1,000 to 200,000, even more preferably from 1,000 to 100,000 and especially from 5,000 to 100;000.

The Dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (hereinafter TPOAC acid) of formula 2:



(2)

wherein T, A, and n are as defined hereinbefore.

The number-average molecular weight (Mn) of the TPOAC acid is preferably not less than 500 and especially not less than 800. It is also preferred that the number-average molecular weight of the TPOAC acid is not greater than 3000 and especially not greater than 2000.

The weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is preferably not less than 7:1, more preferably not less than 8:1 and especially not less than 9:1. It is also preferred that the weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is not greater than 17:1, more preferably not greater than 15:1 and especially not greater than 13:1. Particularly useful effects have been obtained when the weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is from 10:1 to 15:1 and especially from 10:1 to 13:1.

The salts of The Dispersants may be those of any inorganic or organic acid including quaternary ammonium salts, particularly those obtainable by reacting The Dispersant with a dialkylsulphate such as dimethylsulphate or an alkylhalide such as ethylchloride.

Preferably, the salt of The Dispersant is that obtained with an organic or inorganic acid. Examples of suitable acids are hydrochloric, sulphuric and acetic acids. The salt may also be that of an acidic phenol or phenolic polymer. Preferably, The Dispersant is in the form of its free-base.

Particularly useful effects have been obtained when the TPOAC acid is derived from ricinoleic acid and especially 12-hydroxystearic acid, particularly commercially available material which contains a small amount of stearic acid as impurity which acts as a polymerisation terminating or end-cap group in the preparation of the TPOAC acid.

The Dispersants are made by a similar process to Example 7/Agent H disclosed in GB 2,001,083.

The pigment may be from any of the recognised classes of pigments described, for example, in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter heading "Pigments". Examples of inorganic pigments are titanium dioxide, zinc oxide, Prussian blue, cadmium sulphide, iron oxides, vermilion, ultramarine and the chrome pigments, including chromates, molybdates and mixed chromates and sulphates of lead, zinc, barium, calcium and mixtures and modifications thereof which are commercially available as greenish-yellow to red pigments under the names primrose, lemon, middle, orange, scarlet and red chromes. Examples of organic pigments are those from the azo, disazo, condensed azo, thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphendioxazine, quinacridone, perylene, diketopyrrolopyrrole and phthalocyanine series, especially copper phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon black, although strictly inorganic, behaves more like an organic pigment in its dispersing properties. Preferred organic pigments are

phthalocyanines, especially copper phthalocyanines, monoazos, disazos, indanthrones, anthranthrones, quinacridones and carbon blacks.

The printing ink is preferably made by milling the pigment in the non-aqueous medium in the presence of The Dispersant to give a pigment dispersion which is subsequently let down to give the printing ink.

Whereas the non-aqueous may contain up to 2% by weight water it is preferably free from water.

The non-aqueous medium is preferably a substantially non-polar organic liquid.

Substantially non-polar, organic liquids which may be used, either alone or in admixture are aromatic hydrocarbons, such as toluene and xylene, halogenated aliphatic and aromatic hydrocarbons, such as trichloro-ethylene, perchloroethylene and chlorobenzene and particularly aliphatic and aromatic hydrocarbons having at least 6 carbon atoms including mixtures thereof, for example, refinery distillation products and by products.

Preferably, the non-aqueous medium has a polar solubility parameter of not greater than 7.0 $MPa^{½}$ as measured using the method of Hansen, C.M. and Skaarup, K., Journal of Paint Technology, 39 No. 51, 1967, pages 511-514 as described by Patton, T.C. in "Paint Flow and Pigment Dispersion", second edition, Wiley Printerscience, 1979. Examples of non-aqueous media with polar solubility parameters of 7.0 $MPa^{½}$ or less are non-polar organic liquids including mixtures with polar organic liquids wherein the amount of polar liquid is preferably less than 45%, more preferably less than 30%, even more preferably less than 20% and especially less than 10% by weight based upon the weight of the mixture of non-polar and polar organic liquids.

It is especially preferred that the non-aqueous medium with a polar solubility parameter not greater than 7.0 $MPa^{½}$ is an aliphatic hydrocarbon such as those commercially available as Exxsol, Solvesso, Exxon naphtha, Isopar, Pegasol, Lytol and Shellsol.

Particularly suitable non-aqueous media are mixtures of an aliphatic hydrocarbon and a C_{10-30}-aliphatic fatty alcohol which may be linear or branched, saturated or unsaturated. Examples of suitable alcohols are stearyl, lauryl and especially oleyl alcohol.

The dispersion of the pigment in the substantially non-aqueous medium may contain other ingredients which are commonly used in the printing ink industry such as binders, fluidising agents such as those described in GB-A-1508576 and GB-A-2108143, antisedimentation agents, levelling agents and preservatives.

Preferably the ink contains from 2 to 20%, more preferably from 4 to 15% pigm nt based upon the weight of the ink.

As noted hereinbefore, it is preferable to prepare a concentrated dispersion of the pigment which is subsequently diluted to form the final printing ink.

The dispersions typically contain from 5 to 95% by weight of the pigment, the precise quantity depending on the nature of the pigment and the quantity depending on the nature of the pigment and the relative densities of the pigment and the non-aqueous medium. For example, a dispersion which contains an organic pigment, preferably contains from 15 to 60% by weight of the solid whereas a dispersion in which the solid is an inorganic pigment, preferably contains from 40 to 90% by weight of the pigment based on the total weight of dispersion.

The amount of The Dispersion is preferably from 10 to 100%, more preferably from 10% to 70% and especially from 20% to 50% based on the amount of pigment.

The dispersion may be obtained by any of the conventional methods known for preparing dispersions. Thus, the pigment, the non-aqueous medium and The Dispersant may be mixed in any order, the mixture then being subjected to a mechanical treatment to reduce the particles of the pigment to an appropriate size, for example by ball milling, bead milling, gravel milling or plastic milling until the dispersion is formed. Alternatively, the solid may be treated to reduce its particle size independently or in admixture with either the non-aqueous medium or the dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

If a composition containing pigment and The Dispersant is required in dry form, the non-aqueous medium is preferably volatile so that it may be readily removed from the particulate pigment by a simple separation means such as evaporation. It is preferred, however, that the composition is a dispersion.

If the dry composition consists essentially of The Dispersant and a pigment, it preferably contains at least 0.2%, more preferably at least 0.5% and especially at least 1.0% dispersant based on weight of the pigment. Preferably the dry composition contains not greater than 100%, preferably not greater than 50%, more preferably not greater than 20% and especially not greater than 10% by weight based on the weight of the pigment.

The printing ink may additionally contain an RMV modifier which may be a Lewis acid, an organic or inorganic acid or a phenolic compound. Examples of RMV modifiers are acetic, citric, tartaric, toluic and p-naphthoic acids, naphthalene-2-sulphonic acid and p-toluene sulphonic acid; resorcinol and 2-naphthol; alkyl partial esters of phosphorus acids and linear phenolic polymers such as novolak resins. The preferred RMV modifier is a novolak resin, especially those containing a 4-alkyl substituent and particularly those with a C_{1-10}- and especially a C_{4-8}-alkyl group. Useful effects have been obtained with Uravar FN5 as RMV modifier.

The most suitable RMV for any given printing ink can be readily determined using the protocol described in WO 97/15633 which protocol may also be used to establish the optimum amount of RMV modifier. The amount of RMV modifier in the ink is generally not greater than 10%, preferably not greater than 5% and especially not greater than 2%.

In view of the foregoing preferences an especially preferred printing ink according to the first aspect of the invention comprises a pigment, a dispersant of the Formula (1), a substantially non-aqueous medium and a RMV modifier as hereinbefore defined.

The printing inks according to the first aspect of the present invention preferably have a viscosity at 25°C of less than 50cP, more preferably less than 20cP, especially less than 15cP and more especially from 7 to 15cP.

According to a second aspect of the present invention there is provided a process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to the first aspect of the invention.

The preferred inks used in this process are the preferred inks hereinbefore described in relation to the first aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a piezoelectric crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, plastic, an overhead projector slide or a textile material.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper.

Preferred textile materials are natural, synthetic and semi-synthetic materials. Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include, polyamides, polyesters, polyacrylonitriles and polyurethanes.

A third aspect of the present invention provides a substrate printed with an ink according to the first aspect of the present invention, or by means of the process according to the second aspect of the present invention.

A fourth aspect of the present invention provides an ink jet printer cartridge containing an ink according to the first aspect of the present invention.

The invention is further illustrated by the following examples where all references to amounts are in parts by weight unless indicated to the contrary.

Examples 1 to 3: Black Inks

Millbases were prepared having the composition outlined in Table 1 below by milling the components as indicated in the presence of glass beads (3mm, 125 parts) on a horizontal Red Devil shaker for 90 minutes. After milling, the beads were removed and the millbase diluted with oleyl alcohol (7.1 parts, Novol ex Croda Chemicals) and an aliphatic hydrocarbon mineral oil (28.4 parts, Lytol ex Witco) to give a printing ink.

The Receding Meniscus Velocity of the inks (RMV) was measured at 30°C using the method described in WO 97/15633. The results are given in Table 2 below which clearly show that the dispersants according to the present invention (Dispersants (1), (2) and (3)) provide inks which exhibit a superior (higher) RMV compared to Dispersant A (a comparative dispersant which has a weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is 3.5:1 and therefore outside the scope of the present invention).

Table 1

Example	**1**	**2**	**3**	**A**
Millbase	**1**	**2**	**3**	**4**
Regal 250R (pigment)	5.00	5.00	5.00	5.00
Dispersant 1	1.37	-	-	-
Dispersant 2	-	1.37	-	-
Dispersant 3	-	-	1.37	-
Dispersant A	-	-	-	1.71
Solsperse 5000 (fluidising agent)	0.09	0.09	0.09	0.09
Hydrocarbon solvent	3.54	3.54	3.54	3.20
	10.00	**10.00**	**10.00**	**10.00**

Footnote to Table 1

Regal 250R is carbon black pigment ex Cabot Corporation

Dispersant 1 is a 50% solution of PHS/PEI (7:1) in Lytol

Dispersant 2 is a 50% solution of PHS/PEI (10:1) in Lytol

Dispersant 3 is a 50% solution of PHS/PEI (13:1) in Lytol

Dispersant A is a 40% solution of PHS/PEI (3.5:1) in Lytol

Solsperse 5000 is a quaternary ammonium salt of sulphonated copper phthalocyanine ex Zeneca Ltd.

Hydrocarbon solvent is Lytol ex Witco.

Dispersant A is made by the process described in Example 7/Agent H in GB 2 001 083.

Dispersants 1 to 3 are made by a similar process to that described for Dispersant A except that the ratio of poly(12-hydroxystearic acid) to polyethyleneimine (PHS/PEI) is as indicated in parenthesis.

Table 2

Millbase	Dispersant	RMV (mm/sec at 30°C)
1	1	8.9
2	2	10.0
3	3	8.7
4	A	7.9

Footnote to Table 2

Dispersants 1-3 and A are as hereinbefore described in the footnote to Table 1.

Examples 4 to 6 ; Red Inks

Millbases were prepared containing a red pigment by a similar method to that described in Examples 1 to 3 by milling together the components listed in Table 3 below. These millbases were then diluted by adding aliphatic hydrocarbon solvent (27.0 parts, Lytol ex Witco). The RMV was again measured using the method described in WO 97/15633. The results are given in Table 4 and show that those inks prepared using dispersants with a higher PHS to PEI ratio exhibit superior RMV to inks prepared using Dispersant A.

Table 3

Example	**4**	**5**	**6**	**B**
Millbase	**5**	**6**	**7**	**8**
Hostaperm Red E5B02	3.33	3.33	3.33	3.33
Dispersant 1	2.34	-	-	-
Dispersant 2	-	2.34	-	-
Dispersant 3	-	-	2.34	-
Dispersant A	-	-	-	2.92
Hydrocarbon solvent	4.33	4.33	4.33	3.75
	10.0	**10.0**	**10.0**	**10.0**

Footnote to Table 3

Hostaperm Red E5B02 is a red pigment ex Hoechst.

Dispersants 1 to 3, dispersant A and hydrocarbon solvent are as explained in the footnote to Table 1.

Table 4

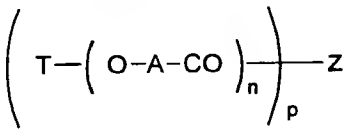
Millbase	Dispersant	RMV (mm/sec at 30°C)
5	1	2.7
6	2	2.9
7	3	4.6
8	A	<1

Footnote to Table 4

Dispersants 1 to 3 and A are as hereinbefore described in the footnote to Table 1.

CLAIMS

1. A drop on demand ink-jet printing ink comprising a pigment, a substantially non-aqueous medium and a dispersant of formula 1



(1)

wherein

T is hydrogen or a polymerisation terminating group;

A is C_{8-20}-linear alkylene;

Z is the residue of a polyamine or polyimine;

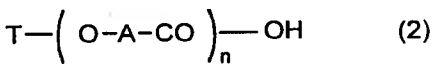
n is from 2 to 10;

p is not less than 2; and

the weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is from 5:1 to 20:1; including salts thereof.

2. A printing ink as claimed in claim 1 wherein the weight ratio of $(T\text{-}(O\text{-}A\text{-}CO)_n\text{-})_p$ to Z is from 9:1 to 13:1.

3. A printing ink as claimed in either claim 1 or claim 2 wherein the dispersant is obtainable by reacting the polyamine or polyimine with an end-capped polyoxyalkylenecarbonyl acid or polyoxyalkenylenecarbonyl acid (TPOAC acid) of formula 2:



(2)

wherein T, A and n are as defined in claim 1.

4. A printing ink as claimed in claim 3 wherein the TPOAC acid is derived from 12-hydroxystearic acid.

5. A printing ink as claimed in either claim 3 or claim 4 wherein the number-average molecular weight of the TPOAC acid is from 800 to 2000.

6. A printing ink as claimed in any one of claims 1 to 5 wher in th number-av rage molecular weight of the polyamine or polyimine is from 5,000 to 100,000.

7. A dispersant as claimed in any one of the preceding claims wherein Z is the residue of polyethyleneimine.

8. A printing ink as claimed in any one of claims 1 to 7 wherein the non-aqueous medium is an aromatic or aliphatic hydrocarbon or mixtures thereof.

9. A printing ink as claimed in claim 8 which additionally comprises a C_{10-30}-aliphatic fatty alcohol.

10. A printing ink as claimed in any one of claims 1 to 9 wherein the non-aqueous medium has a solubility parameter of 7.0 $MPa^{½}$ or less.

11. A printing ink as claimed in any one of claims 1 to 10 which additionally comprises a fluidising agent.

12. A printing ink as claimed in any one of claims 1 to 11 which additionally comprises a Receding Meniscus Velocity (RMV) modifier.

13. A printing ink as claimed in claim 12 where the RMV modifier is a linear phenolic polymer.

14. A printing ink according to any one of the preceding claims wherein the ink has a viscosity at 25°C of less than 50cP.

15. A process for printing an image on a substrate comprising applying thereto by means of a drop on demand ink jet printer a printing ink according to any one of the preceding claims.

16. A substrate printed with an ink according to any one of claims 1 to 14, or by means of the process according to claim 15.

17 An ink jet printer cartridge containing an ink according to any one of claims 1 to 14.